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Condensation Reactions
with Ethyl Oxomalonate

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CONDENSATION REACTIONS WITH
ETHYL OXOMALONATE

BY

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B. A. University of Illinois, 1909

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF ARTS

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

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UNIVERSITY OF ILLINOIS
THE GRADUATE SCHOOL

June 1, 1911

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Lloyd Francis Nickell

ENTITLED Condensation Reactions of Ethyl Oxomalonate,

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Arts.

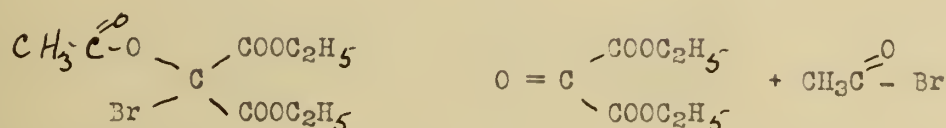
Richard D. Curtis
In Charge of Major Work
W. A. Noyes
Head of Department

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Recommendation concurred in:

} Committee
on
Final Examination

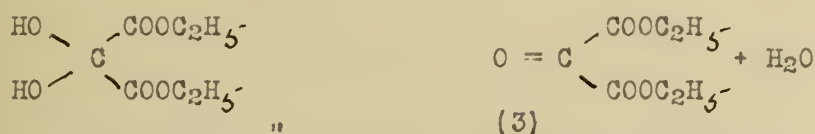
INTRODUCTION.

Ethyl oxomalonate, $O = C \begin{matrix} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{matrix}$ was first prepared and identified by Anschutz and Parlato (1) by distilling ethyl acetylbromtartronate under reduced pressure.

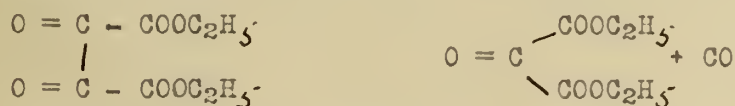


" (2) Conrad and Bruckner prepared the same product previously by the same method but had not recognized it as such.

" Anschutz and Parlato also prepared ethyl oxomalonate by distilling ethyl dihydroxymalonate under reduced pressure:



" (3) Later, Anschutz and Pauly prepared oxomalonate ester by subjecting dioxosuccinic ester to vacuum distillation:



The product obtained from each of the above reactions, as might be expected, was impure due to the reversal of the above reactions. Curtiss and Spencer, (4) however, were able to obtain the pure methyl ester by treating methyl dihydroxymalonate with an excess of phosphorus pentoxide, and distilling off the resulting green oil under reduced pressure. Curtiss and Strachan (5)

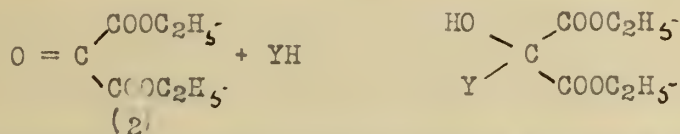
(1) Berichte 25, 3616
(2) Berichte 24b, 3000
(3) Berichte 27, 1305

(4) Jour. Amer. Chem. Soc. 31, 1054
(5) Jour. Amer. Chem. Soc. 33, 397.

secured a good yield of the pure ethyl oxomalonate by the same method.

(1)

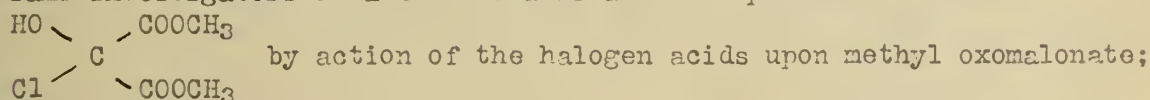
Chemically, ethyl oxomalonate is very reactive, uniting with water with great avidity to form ethyl dihydroxymalonate. In an analogous manner compounds possessing dissociable hydrogen react with ethyl oxomalonate:



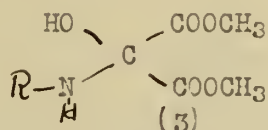
Curtiss and Spencer obtained such products by the action of the alcohols with methyl oxomalonate:



The same investigators obtained unstable addition products such as



and by treating the same ester with aniline and ammonia, secured products of this structure:



Curtiss and Strachan obtained similar products by the action of halogen acids, urethane, and urea with ethyl oxomalonate. Curtiss, Hill and Lewis succeeded in making the same type of compounds by the reaction of ethyl oxomalonate with ortho, meta, and para toluidines as well as with aniline and alcohols.

By means of a modification of the Friedel and Craft synthesis, Michel and Guyot condensed both ethyl and methyl oxomalonate with the tertiary aromatic amines, dimethylaniline, diethylaniline, methylethyylaniline and ethylbenzylaniline. The reaction in each case was upon the para hydrogen of the amine and the reactive ketone group of oxomalonate, according

(1) Anschutz and Parlato, Berichte 25, 3616

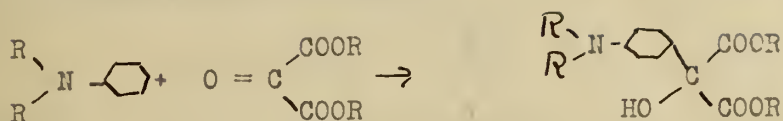
(2) Jr. Am. Chem. Society 31, 1053

(3) Jr. Am. Chem. Society 35, 397

(4) Jr. Am. Chem. Soc. 33, 400

(5) Ph.D. Thesis Univ. of Nancy 1911

to the following general equation:



They found that the same products resulted when the dihydroxymalonate was used in place of the oxomalonate in the synthesis.

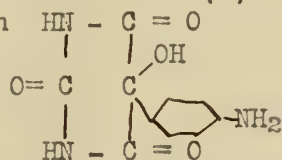
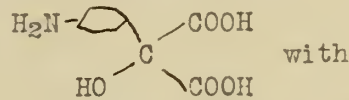
The same reactions were tried with the secondary aromatic amines, monomethyl and monoethyl orthotoluidines. According to Michel and Guyot the reaction was as follows:



These dialkylparaamino phenyltartronic esters, and the paramonoalkylamino-meta methyl-phenyl-tartronic esters are colorless, stable, crystalline compounds melting from 31.5° to 110.5°.

The structure of these compounds is based upon the fact that by saponification with potassium hydroxide and oxidation with copper sulphate solution, glyoxylic acids of the type $R_2NC_6H_4 - CO - COOH$ are formed.

These acids were identified by comparison with the acids obtained by oxidation of tartronic acids of the structure (1) with mercuric oxide. The structure of these tartronic acids in turn is shown from their formation by saponification of aniline alloxan (2)

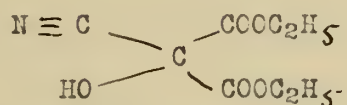


and similar substances. The structure of aniline alloxan is shown by its giving para toluidine when distilled with lime. (3)

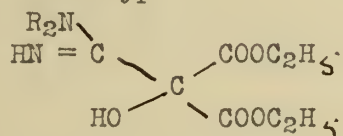
All of these condensation reactions of compounds having dissociable

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- (1) D. R.P. 117021, Frdl. VI, 166.
 (2) D. R.P. 112174, Frdl. VI, 174.
 (3) Gaz. Chemie It. 17, 412.

hydrogen with oxomalonate have been upon the reactive carbonyl group of the latter. We have tried the reaction of anhydrous hydrogen cyanide upon ethyl oxomalonate, obtaining the nitrile, ethyl cyan-tartronic ester:



This compound contains the very reactive, triple-bonded, nitrile group and should react with ammonia and the amines to form amidines, and substituted amidines of the type:



We have succeeded in making ethyl cyantartronate and in obtaining addition products by the action of dipropylamine, benzyl amine, and ammonia gas upon it. We have also tried the action of triethyl amine upon ethyl cyantartronate.

EXPERIMENTAL PART.

Preparation of Ethyl Cyantartronate.

Anhydrous hydrogen cyanide was prepared according to the method
(1)
of Wade and Panting. The gas was passed through two calcium chloride U tubes and then through a U tube of phosphorus pentoxide before being condensed. The vent to the flue was properly protected by a calcium chloride tube.

5.73 grams of pure ethyloxomalonate were put into a flat bottomed sample tube of 35 c.c. capacity. The outlet tube was carefully protected from atmospheric moisture by calcium chloride and phosphorus pentoxide. An equal volume of anhydrous hydrogen cyanide was then distilled into the ketone, forming two distinct layers.

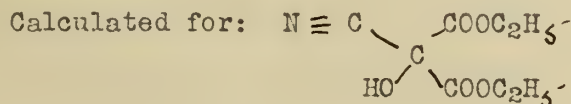
(1) Jour. Chem. Soc. 1898, p. 255

The layers were mixed by shaking and without any apparent heat effect, or color change in the ketone. The mixture was kept at room temperature (25°) for 24 hours. The yellow color slowly weakened and finally entirely disappeared. The speed of this reaction is greatly affected by small changes of temperature. At 18°-19°, 72 hours are required to complete the reaction as indicated by the complete disappearance ^{of color} while at 30° 12 hours is sufficient. No appreciable volume change accompanies this reaction.

When the reaction was complete the tube was placed in a desiccator over sulphuric acid together with a dish containing stick sodium hydroxide, and the desiccator evacuated to remove the excess hydrogen cyanide. The tube was then removed and weighed. 0.89 gram had been added. Results from several experiments are given below:

wt. of ketone	wt. of HCN	Theory (1 mol)
5.72	0.89	0.88
9.11	1.42	1.41
8.77	1.23	1.25

The oil was then shaken with ice water until the washings gave no immediate precipitate with silver nitrate solution, dried over fused calcium chloride and analyzed.



C, 47.76; H, 5.47; N, 6.96;

Found: C, 47.82, 48.28; H, 5.74 - N, 7.09, 6.99

Molecular weight determinations were made by solution in benzene according to the freezing point method and gave results as follows:

Wt. of C_6H_6	Wt. of Ethyl cyantartrionate	ΔT_F	M	Theory
15.13	0.6491	0.889°	243	201
15.40	.5610	0.778°	234	

A more satisfactory method of washing ^{ethyl}cyantartronate free from the excess hydrogen cyanide is to dilute with 5 or 6 volumes of dry ether and evacuate in a desiccator. After repeating two or three times, no odor of hydrogen cyanide can be detected in the tartronate.

Properties of Ethyl Cyantartronate.

Ethyl cyantartronate is a colorless oil having the consistency of concentrated sulphuric acid. Its odor is not unpleasant. It has a specific gravity of 1.1621 at 30°/30°. Upon long standing it gradually assumes a yellow-amber color without the loss of hydrogen cyanide. Although it cannot be distilled, owing to decomposition into ethyl oxomalonate and hydrogen cyanide, it can be heated to 90° before any noticeable decomposition occurs. It is easily soluble in ether, benzene, alcohol, acetone, chloroform, and ethyl acetate, but is insoluble in ligroin and water.

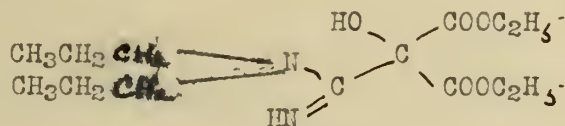
Alkali solutions dissolve it readily giving a deep yellow color. Dilute sulphuric acid precipitates an oil from this solution. Dilute hydrochloric acid does not affect ethyl cyantartronate, but it dissolves to a yellow color in 30% acetic acid. Upon dilution with water an oil precipitates which redissolves again in 30% acetic acid. A solution of the oil in absolute ether (1:6) will effervesce slightly when metallic sodium is added. The solution gradually becomes yellow. In 1 1/2 hours the solution becomes filled with white needle-like crystals which go into solution again by heating with the hand. These crystals will dissolve in water, thus forming an oil. They are deliquescent. When left in the original solution 24 hours, they decompose, leaving a brown tarry residue which is insoluble in ether.

Reaction of Ethylcyantartronate with Dipropyl Amine.

If dipropyl amine is added to ethyl cyantartronate drop by drop, a

vigorous action with a rise of temperature to 70°-80° takes place. The result is a dark reddish brown sirup. If, however, the reaction is allowed to run in a freezing mixture a fairly stable product is obtained. 1.76 grams of ethyl cyantartrionate were dissolved in 2 c.c. of dry ether and a solution of 0.888 gram (1 mol.) of dipropyl amine in 5 c.c. of ether was added drop by drop, the flask in which the reaction occurred being kept in a freezing mixture. In less than one minute white crystals began to separate. After the reaction was completed, these crystals were dried on a porous plate. They were then redissolved in ether, the ether evaporated on a 50° water bath to 1/3 volume, and the addition product recrystallized from this solution by cooling. The crystals were filtered off, washed twice with a small amount of cold, dry ether and dried in a vacuum desiccator over calcium chloride. The desiccator was kept in the ice box. The product was dried three hours, the melting point determined and then analyzed.

Calculated for:



C, 55.62;

H 8.67;

II, 9.27;

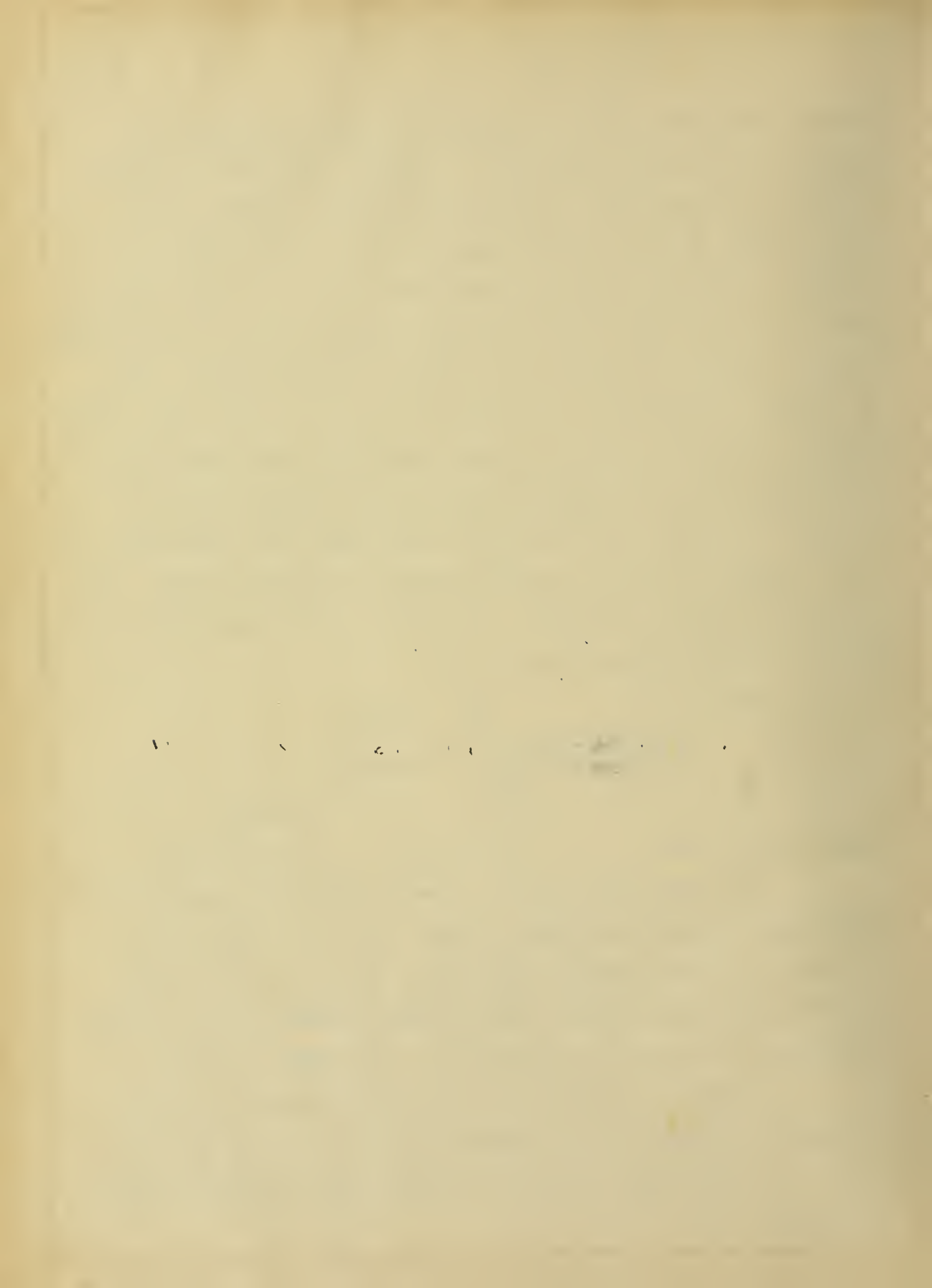
Found C, 55.45; 54.97;

H. 8.70, 8.77;

N, 9.14, 9.25;

The dipropyl amine addition product of ethyl cyantartionate is a white crystalline substance melting at 72.5° - 73°. It is easily soluble in benzene, chloroform, acetone, acetic ether, and methyl alcohol; fairly soluble in water, ethyl alcohol, ether, and CCl₄; slightly soluble in carbon bisulphide, and ligroin, but readily soluble in the latter on heating.

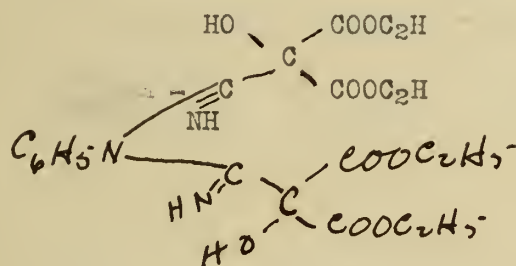
If kept in a desiccator and in the ice box these crystals are stable for several days, but if exposed to the air or kept in a warm place (25°) they decompose in a few hours to a reddish brown gum having an aromatic cinnamon-like odor.



Reaction of Ethyl Cyantartronate with Benzyl Amine.

0.739 gram of benzyl amine was dissolved in 2 c.c. of dry ether and added drop by drop to a solution of 1.389 grams of ethyl cyantartronate in 2 c.c. of dry ether. The reacting mass was kept at -15° . White crystals separated immediately. These were filtered off and washed once on the filter with cold, dry ether. They were then put in a vacuum over calcium chloride and kept at 10° for two hours. The product had yellowed slightly on the surface. The melting point was not sharp. It softened at 52° - 53° and melted to a clear yellowish liquid at 55° - 56° . The substance was then analyzed.

Calculated for:



	C 54.19	H 6.13	N 8.27
Found	54.14, 54.47	5.98, 6.15	8.20, 8.11

The benzyl amine addition product of ethyl cyantartronate is easily soluble in alcohol, and ethyl acetate; extremely soluble in acetone chloroform, methyl alcohol, nitrobenzene, and benzene, dissolving in the latter with marked absorption of heat; fairly soluble in xylene, and ether; and slightly soluble in carbon bisulphide and ligroin.

A slightly different method was used in the preparation of this product than that used for the dipropyl amine addition product of ethyl cyantartronate because of a greater solubility of the former in ether.

The benzyl amine addition product of ethyl cyantartronate is insoluble in water, but slowly disappears forming a turbid emulsion. This is accompanied by a slight odor of hydrogen cyanide, and soon droplets of an oil

appear.

Concentrated sulphuric acid dissolves it instantly forming a slightly yellow solution. This solution gives a yellow oil that floats on top when diluted with water. A benzene solution of the benzyl amine addition product gives an immediate white precipitate when treated with dry hydrogen chloride gas.

The benzyl amine addition product of ethyl cyantartronate decomposes like the dipropyl amine addition product when allowed to stand over calcium chloride at 25° for 24 hours. The decomposition gives a sticky, reddish brown tar of aromatic, cinnamon odor.

Action of Dry Ammonia Upon Ethyl Cyantartronate.

At room temperature dry ammonia acts very vigorously upon ethyl cyantartronate, giving a red, tarry product.

1.97 grams of ethyl cyantartronate were put in a 35 c.c. flat bottomed sample tube provided with a stirring apparatus, and protected from the air by a calcium chloride tube. Dry ammonia was then slowly admitted, the reacting mass being kept at -15°. As soon as the ammonia strikes the surface a white scum is formed on the ethyl cyantartronate. This was well stirred up, more ammonia was admitted, and the operation repeated. A mucilage like mass soon formed on the stirrer. Care had to be taken at this stage to keep a hard mass from forming on the stirrer. All the substance had to be well stirred as a residue of the ethyl cyantartronate in any part of the mass starts decomposition soon after the completion of the reaction. In 30 minutes the contents of the tube had become a white dry powder, indicating the completion of the reaction. Care had to be taken that an excess of ammonia was not admitted as this starts decomposition. The apparatus was then weighed.

0.100 gram of ammonia had been added.

Two such experiments gave the following results:

	Wt. of ethyl Cyantrarbonate	wt. of NH_3 added	Theory for 1 mol. of NH_3
I	1.970 g	0.100 g	0.105
II	0.630	0.052	0.053

These results indicate that 1 mol of ammonia had been added to form the addition product.

A more satisfactory method of preparing the ammonia addition product of ethyl cyantrarbonate is as follows: 0.727 gram of ethyl cyantrarbonate was dissolved in 5 c.c. of dry ether. The solution was put in a 35 c.c. flat bottom sample tube and protected from atmospheric moisture by a calcium chloride tube. 0.0614 (1 mol) of ammonia was collected in an azotometer over mercury, and added slowly to the above solution, the reaction being kept at -15° . White crystals began to separate in two minutes when one-tenth of the ammonia had been added. In ten minutes all the ammonia had been added. The solution had formed a white paste. This paste was put on a filter and the excess ether filtered off, care being taken not to suck any air through the mass. It was washed on the filter once with ether, quickly transferred to a calcium chloride desiccator, the desiccator evacuated to 50 mm. and kept at 10° .

The ammonia addition product of ethyl cyantrarbonate is very unstable. Exposure to the moisture of the air for one minute starts decomposition and in ten minutes a thick, reddish paste results. It decomposes in 30 minutes when kept at room temperature (25°) in a vacuum over calcium chloride. When made by the above method, however, and all possible care exercised, it can be kept over calcium chloride at 10° for 2 - 3 hours

without noticeable decomposition.

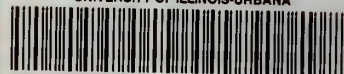
This substance is very soluble in benzene and alcohol; slightly soluble in ether and ligroin. It crystallizes from ether in balls of radiating needles. It deliquesces in the air emitting the odors of ammonia and hydrogen cyanide. When heated it softens at 45° - 46° and melts to a clear colorless liquid without evolution of gas at 49° -49.5°.

Owing to its extreme instability this product has not been analyzed as yet.





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